The Children's Cancer Research Foundation,
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8-Arylpurines and Their Ultraviolet Absorption Spectra (1)

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Dehydrocyclization of 4-amino-5-arylamidopyrimidines in polyphosphoric acid to 8-arylpurines was further investigated. Various other 8-arylpurines were synthesized by this new procedure in high purity and yield. The ultraviolet absorption spectra of the arylpurines and the corresponding acylamidopyrimidines were measured at pH 1, 7, and 13 at 0.1 molar ionic strength. The spectra of the purines resemble those of the corresponding acylamidopyrimidines and, to a lesser extent, the corresponding 4,5-diaminopyrimidines. The bathochromic shifts caused by different substituting groups in monosubstituted purines, in general, parallel the inductive effect of the substituting groups. The hyperchromicity and the inductive constant of the substituting groups assume a linear relationship, for substitution at either the 2 or 6 position. These changes in the wave length of maximum absorption and in the molar extinction coefficient caused by 2, 6 and 8 substitutions of the purines reported here are in agreement with previous studies by Mason.

Recently the dehydrocyclization of 4-amino-5-acylamidopyrimidines to purines with polyphosphoric acid was reported (2). The polyphosphoric acid procedure was found to be superior to other processes (3a-g) employed, which generally yield products difficult to purify. The versatility of this new procedure was demonstrated by the preparation of other 8-arylpurines in high purity and yield thereby confirming the previous observation that substitutions on the 2 and 6 positions of the pyrimidine ring and on the *para* position of the phenyl ring had little or no influence on cyclization (2). The quantitative ultraviolet absorption spectra of the pyrimidines and purines synthesized were measured at pH 1, 7, and 13 at 0.1 molar ionic strength.

Acylation of 4,5-diaminopyrimidines gave 4-amino-5-acylamidopyrimidines (2, 4a-c) (Table I) which were purified and analyzed, and appeared as single spots on paper chromatograms. Cyclization of these acylpyrimidines to 8-arylpurines was performed in polyphorphoric acid at 160-170° (5) as previously described (2). One recrystallization suffices to give pure compounds which appear as single spots on paper chromatograms (Table II).

As the corresponding 4,5-diaminopyrimidines were not available, two substituted purines were prepared by other methods in order to study spectral shifts. Thiation of 2-methyl-6-hydroxy-8-phenylpurine (XX) with phosphorus pentasulfide gave 2-methyl-6-mercapto-8-phenylpurine (XVIII), which was dethiated with nickel catalyst to 2-methyl-8-phenylpurine (XIX).

The spectra of the arylamidopyrimidines (Table III), and of the corresponding 4,5-diaminopyrimidines (6a-e) showed close resemblance except that benzoyl substitution on the 5-amino group caused a hypsochromic shift. Consequently, two narrow bands are

observed around the regions of 235 and 265 mμ. Concerning the molecular extinction coefficient, the absorption in alkaline medium usually is lower than that in the neutral and acidic media. A marked bathochromic effect relative to that of the parent compound, 4-amino-5-benzamidopyrimidine, is produced by the mercapto group in the 2 and/or 6 position. Other substitutions at position 2 and/or 6 produced little or no spectral shift.

The purine spectra, as shown in Table IV, are generally composed of two bands, occasionally three, in the regions of 210-294 and 286-402 mμ and they closely resemble those of the corresponding acyl-
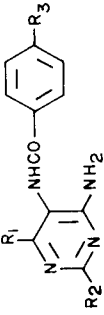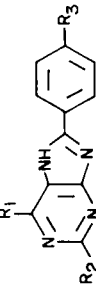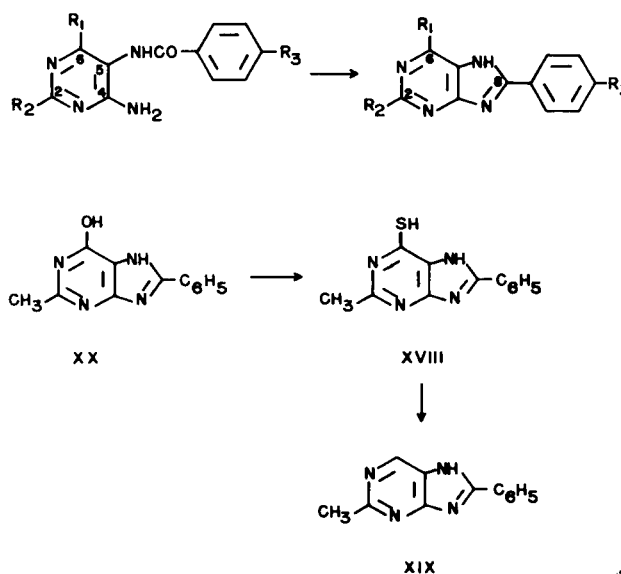
TABLE I

4-Amino-5-Arylamidopyrimidines

Structure: R_1, R_2 (on pyrimidine ring), $-NHCO-$ phenyl with R_3 para; NH_2 substituent.

Compound	R_1	R_2	R_3	Formula	Solvent Recryst. (a)	Yield (b) %	M.P. (dec.) °C	Required % C	H	N	S	Found % C	H	N	S	R_f A	R_f B
I	CH_3	NH_2	H	$C_{12}H_{13}N_5O$	A	53	268-269	59.2	5.4	28.9		58.7	5.7	28.8		0.59	0.66
II	H	NH_2	H	$C_{11}H_{11}N_5O \cdot 1/2H_2O$	A	24	130-131 (c)	55.4	5.1	29.4		55.2	5.2	29.3		0.47	0.64
III	OH	H	H	$C_{11}H_{10}N_4O_2 \cdot 1/2H_2O$	C	83	305-307	55.2	4.6	23.4		55.4	4.7	23.0		0.49	0.37
IV	OH	SH	H	$C_{11}H_{10}N_4O_2S \cdot H_2O$	C	59	(d)	47.1	4.3	20.0	11.4	46.7	4.7	20.0	11.2	0.58	0.30
V	OH	OH	H	$C_{11}H_{10}N_4O_3$	B	44	> 350	53.7	4.1	22.8		53.4	4.0	23.0		0.58	0.21
VI	OH	NH_2	H	$C_{11}H_{11}N_5O_2$	B	69	317 (e)	53.9	4.5	28.6		53.6	4.7	28.5		0.46	0.34
VII	OH	NH_2	NO_2	$C_{11}H_{10}N_6O_4$	B	60	> 350	45.5	3.5	29.0		45.3	3.6	28.7		0.35	0.31
VIII	NH_2	NH_2	H	$C_{11}H_{12}N_6O \cdot 1/2H_2O$	A	41	243-245 (f)	52.1	5.2	33.2		51.7	5.0	33.6		0.39	0.38

(a) A = Water; B = 50% Acetic Acid; C = Methyl Cellosolve-Ether. (b) Purified yield. (c) Reported 213-214°, cf. Ref. 13. (d) The compound turns black at 270°, and does not melt above this temperature. (e) Reported 318-319°, cf. Ref. 4a. (f) Reported for free base 274-275°, cf. Ref. 13.

TABLE II

8-Arylpurines Synthesized With the Polyphosphoric Acid Method

Structure: purine ring with R_1, R_2, NH, N; 8-aryl phenyl bearing R_3.

Compound	R_1	R_2	R_3	Formula	Procedure	Solvent Recryst. (b)	Yield (c) %	M.P. (dec.) °C	Required % C	H	N	Cl	S	Found % C	H	N	Cl	S	R_f A	R_f B
IX (a)	CH_3	SH	H	$C_{12}H_{10}N_4S$	B	A	56	346-347	59.5	4.2	23.1		13.2	59.3	4.5	22.7		13.4	0.41	0.35
X	CH_3	NH_2	H	$C_{12}H_{11}N_5 \cdot 1/2H_2O \cdot HCl$	A	A	94	> 350	53.2	4.8	25.9	13.1		52.9	5.0	26.0	13.0		0.48	0.72
XI	H	NH_2	H	$C_{11}H_9N_5 \cdot HCl$	A	B	52	333 (d)	53.3	4.1	28.3	14.3		53.2	4.1	28.2	14.2		0.38	0.63
XII	OH	H	H	$C_{11}H_8N_4O$	B	C	72	> 350 (e)	62.3	3.8	26.4			62.0	4.0	26.7			0.45	0.52
XIII	OH	SH	H	$C_{11}H_8N_4OS$	B	C	31	220-225 (f)	54.1	3.3	22.9			53.8	3.7	22.5			0.55	0.46
XIV	OH	OH	H	$C_{11}H_8N_4O_2 \cdot 1/2H_2O$	A	A	40	> 350 (g)	55.7	3.8	23.6			55.6	3.7	24.6 (j)			0.40	0.29
XV	OH	NH_2	H	$C_{11}H_9N_5O \cdot 1/2H_2O \cdot HCl$	A	A	64	> 350 (h)	48.4	4.1	25.7	13.0		48.2	4.1	26.2	12.7		0.29	0.36
XVI	OH	NH_2	NO_2	$C_{11}H_8N_6O_3 \cdot H_2O$	A	A	40	> 350 (h)	45.5	3.5	29.0			45.5	3.5	28.7			0.10	0.33
XVII	NH_2	NH_2	H	$C_{11}H_{10}N_6 \cdot H_2O \cdot HCl$	A	A	96	342-343 (i)	47.1	4.7	29.9	12.6		47.2	4.6	29.9	12.8		0.30	0.62

(a) The corresponding pyrimidine could not be purified. (b) A = 2 N Hydrochloric Acid; B = 1 N Hydrochloric Acid; C = Water. (c) Purified yield. (d) Reported for free base 265-268°, cf. Ref. 3b. (e) Cf. Ref. 3e. (f) Cf. Ref. 3e-g. (g) Cf. Ref. 3g. (h) Cf. Ref. 3a. (i) Cf. Ref. 3d. (j) This value for nitrogen was the best analysis available.

TABLE III

Ultraviolet Absorption Spectra of 4-Amino-5-Arylamidopyrimidines

Compound	R_1	R_2	R_3	pH 1		pH 7		pH 13	
	(as in Table I)			λ max (mμ)	ϵ max	λ max (mμ)	ϵ max	λ max (mμ)	ϵ max
I	CH_3	NH_2	H	229.5	24,000	228	18,600	228	17,100
				268	8,000	281	8,800	282.5	8,300
II	H	NH_2	H	230	22,800	230	21,600	225 (a)	16,450
				275 (a)	7,000	275 (a)	6,400	290	7,600
III	OH	H	H	258	9,250	258	9,200	260 (a)	6,900
IV	OH	SH	H	227	12,400	225	12,700	237 (a)	16,300
				284	19,100	284	18,600	290	14,000
V	OH	OH	H	229	14,600	227.5	14,500	230 (a)	14,300
				263	19,400	263	20,100	266	16,700
VI	OH	NH_2	H	236	13,600	232 (a)	13,600	234 (a)	14,400
				265	20,000	267	15,800	262.5	11,300
VII	OH	NH_2	NO_2	264.5	28,700	267	24,800	262.5	20.600
VIII	NH_2	NH_2	H	215	31,200	215	29,600	236 (a)	16,100
				237 (a)	15,800	238 (a)	14,800	267	12,400
				272	19,200	272	18,200		

(a) Shoulder.

pyrimidines and, to a lesser extent, the corresponding 4,5-diaminopyrimidines (6a-e). Platt (7a, b) pointed out the resemblance of the spectra of indene and azaindenes to those of styrene (8) and naphthalene in which the first two transitions in each case are longitudinal and transverse. From comparison of the spectra of purines with azaindenes, Mason (9) assigned the two absorption bands of purines, at 260 and < 220 mμ for the unsubstituted purine, as X (long wave length) and Y (short wave length), respectively. The X band, which is probably an envelope covering the first two transitions, consists of an intense and a weak component, due principally to longitudinal polarization with smaller contribution from a transverse polarization. Since substitutions at the 6 and 8 positions are transversely and longitudinally disposed with respect to the longer axis of the molecule, they resulted in lowering the transitional energy of the weak and intense components of the X band, respectively. Substitution in the 2 position, which is oriented at a 30° angle to the longer axis, lowered the transitional energy of both components (9). Thus, the increase of bathochromic shifts, with monosubstitution at various positions in purine, by an electron-donating group was found to be in the order: 6 < 8 < 2 (9).

In the present study on the 8-arylpurines, in the preceding report (2) and in studies on other purines (9), the bathochromic shifts by various substituting groups in monosubstituted purines, in general, parallel the inductive effect (electronegativity) (10a-c) of the groups. In the 8-arylpurine series here considered, the 8-phenyl group is always present except in compound XVI (8-p-nitrophenyl-). The

bathochromic shifts caused by 6 substitution are thus in the order: OH < NH_2 < CH_3 < H < SH and NH_2 < OH < CH_3 = H < SH at pH 1 and 13, respectively. The shifts caused by the substitution on the 2 position are in the order: H < CH_3 < NH_2 for both pH 1 and 13. The abnormally large bathochromic shift caused by the mercapto group is probably due to the polarisability (10a) of the C-S bond.
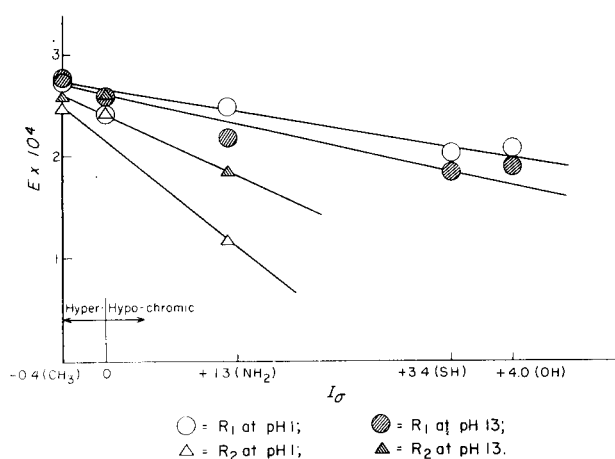

Fig. 1. Change of Molecular extinction Coefficient (E) of X Band vs. Inductive Constant (I σ) of the substituting groups in the 8-Arylpurines.

TABLE IV

Ultraviolet Absorption Spectra of 8-Arylpurines

Compound	R_1	R_2 (as in Table II)	R_3	pH 1 λ max (mμ)	ε max	pH 7 λ max (mμ)	ε max	pH 13 λ max (mμ)	ε max
IX	CH₃	SH	H	257 (a, b)	10,400			259	29,800
				294 (b)	38,600			345	14,400
				384 (b)	9,440				
X	CH₃	NH₂	H	253	26,600	237	16,800	238	19,800
				330	15,200	324.5	20,100	327	20,500
XI (c)	H	NH₂	H	210	20,200	215	19,000	237.5	19,000
				256	23,400	237.5	15,000	328	18,700
				332.5	11,800	329	17,800		
XII	OH	H	H	234	11,100	235	11,700	236	18,700
				286	21,400	286	21,400	303	19,700
						297 (a)	19,000		
						312 (a)	8,000		
XIII	OH	SH	H	232.5 (a)	13,800	222.5 (a)	16,000	241	17,700
				296	19,100	299	18,400	315.5	16,800
XIV	OH	OH	H	236 (b)	9,700			233	19,900
				296 (b)	18,800			241	20,100
								320	15,100
XV	OH	NH₂	H	238	13,900	226	13,550	237	18,660
				266	10,600	274 (a)	11,100	318	17,200
				305	15,900	305	16,300		
XVI	OH	NH₂	NO₂	216	13,000	233 (a)	12,000	251	16,900
				256	16,000	258	16,100	263 (a)	15,350
				345	6,750	357	5,700	402	6,500
XVII	NH₂	NH₂	H	227	21,000	228	22,700	241.5	23,200
				315	24,800	314	23,600	321	21,200
XVIII	SH	CH₃	H	261	25,600			(d)	
				350	23,100				
XIX	H	CH₃	H	238	16,800	233	13,400	233	19,100
				305	24,800	296 (a)	25,600	308	26,000
						302	26,700	322 (a)	16,500
						315 (a)	15,200		

(a) Shoulder. (b) In 2 N hydrochloric acid. (c) Absorptions at pH 1.0, 6.50 and 11.40 were reported (Ref. 9) in which the λ max and ε max given are in good agreement with figures shown in this Table. (d) Unstable.

Mason further proposed that the pyrimidine nucleus of purine exerts an electron-attracting effect on the imidazole nucleus, giving rise to a longitudinal dipole where the pyrimidine nucleus is "-" and the imidazole "+". Electron-donating substitution, by virtue of mesomeric effect, which would enhance the dipole when placed in the 8 position, causes a hyperchromic shift relative to that of the parent compound. This effect again occurs throughout the 8-arylpurines series studied. An electron-donating substitution on the 6 position would enhance a transverse dipole across the pyrimidine nucleus of the purine and cause hyperchromic effects, but to a lesser degree. Such substitution in the 2 position, which is in the reverse direction to both longitudinal and transverse dipoles, exerts hypochromic effects. Thus, the hyperchromic effect by an electron-donating substituent at various positions in purine, was found to be in the order: 2 < 6 ≦ 8 (9).

For the monosubstituted 8-arylpurines considered here and in the preceding report (2), the hyperchromic effects observed are in the order:

SH < OH < H < NH₂ < CH₃
and
SH < OH < NH₂ < H < CH₃
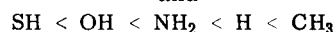
at pH 1 and 13, respectively. By substitution at the 2 position, the hyperchromic effect is in the order: NH₂ < CH₃ < H. There is a linear relation between the hyperchromicity and the inductive constant (10b) of substituent on either the 2 or 6 positions, as shown in Figure 1. The mercapto group

is hypochromic, but causes a strong bathochromic shift.

Because the 8-phenyl group in purines gives rise to a marked bathochromic shift, the Y (short wave length) band of the 8-arylpurines is near 230 mμ and the bathochromic effect caused by the 6-substitution is in the order of, $NH_2 < OH < H = CH_3$ and $H = CH_3 < OH < NH_2 < SH$ at pH 1 and 13, respectively. The hyperchromicity runs: $OH < H < NH_2 < CH_3$ and $H < SH \leq OH < CH_3 < NH_2$ at pH 1 and 13, respectively. In the 2-substituted purines, the bathochromic effect is in the order: $H < CH_3 < NH_2$ and $H = CH_3 < NH_2$ at pH 1 and 13, respectively, while the hyperchromic effect is in the order: $H < CH_3 < NH_2$ and $H < NH_2 \leq CH_3$ at pH 1 and 13, respectively.

Correlation of substitutions to the spectra at pH 7 was not made because, in neutral medium, an 8-arylpurine most probably exists in more than one ionic species. The 8-phenyl group causes bathochromic shift in all the purines studied and it also minimizes the difference in wave length change of maximum absorption by various 2 and 6 substitutions. The changes in the wave length of maximum absorption and in the molecular extinction coefficient induced by 2, 6 and 8 substitutions reported here are in agreement with Mason's findings (9). It has also been found that the effects of di- and tri-substitutions on purines are not additive, as previously observed (9).

EXPERIMENTAL (11)

4-Amino-5-arylamidopyrimidines.

These compounds were prepared according to the previously published procedure (2).

2,4-Diamino-6-hydroxy-5-(4'-nitrobenzamido)pyrimidine (VII).

To a suspension of 16.8 g. of sodium hydrogen carbonate in 50 ml. of water, 4.78 g. of 2,4,5-triamino-6-hydroxypyrimidine sulfate was added, with stirring. As the evolution of carbon dioxide subsided, a solution of 3.71 g. of p-nitrobenzoyl chloride in 50 ml. of ethyl acetate was poured into the mixture, which was stirred continuously at 0° for 1.5 hours. At the end of this period, 50 ml. of water was added and the reaction mixture was acidified to pH 5, with 6 N hydrochloric acid. The ethyl acetate was evaporated in a current of nitrogen; the precipitate was filtered and washed with water and ether, to give 5.8 g. of crude compound. An orange solid was obtained by recrystallizing from 80 parts of 50% acetic acid.

8-Arylpurines.

The purines were prepared according to the two general procedures, A and B, described previously (2).

2-Amino-8-phenylpurine (XI).

This compound was prepared as in procedure A (2), by heating the pyrimidine and polyphosphoric acid at 110-120° for 2 hours.

6-Hydroxy-8-phenylpurine (XII).

Three grams of 4-amino-6-hydroxy-5-benzamidopyrimidine were dissolved in 15 ml. of 1 N sodium hydroxide and the solution was evaporated to dryness in vacuo. To the residue and 25 g. of phosphorus pentoxide, cooled to 0°, 18 ml. of 85% phosphoric acid was added and the mixture was heated to 160-170° and stirred for 1 hour. The isolation of the purine was accomplished as in Procedure B (2). This crude material was dissolved in 100 ml. of 0.1 N sodium hydroxide and acidified to pH 5 with 6 N hydrochloric acid. The pre-

cipitate, 2.0 g. (72%), is pure enough for subsequent use. An analytical sample was obtained by extraction with water in a Soxhlet extractor for 24 hours.

Direct cyclization of 4-amino-6-hydroxy-5-benzamidopyrimidine resulted in a low yield of the purine and complete purification could not be attained.

2-Amino-6-hydroxy-8-(4'-nitrophenyl)purine (XVI).

This compound was prepared as in procedure A (2) by heating the pyrimidine and polyphosphoric acid at 140-150° for 3 hours. The product was recrystallized from 2 N hydrochloric acid and washed thoroughly with water and ether.

2-Methyl-6-mercapto-8-phenylpurine (XVIII).

A mixture of 1.6 g. of 2-methyl-6-hydroxy-8-phenylpurine (2), 6.5 g. of phosphorus pentasulfide, and 50 ml. of dry pyridine was refluxed under anhydrous conditions for 1 hour. The pyridine was removed in vacuo, 70 ml. of water was added to the residue, the mixture was boiled for 15 minutes and filtered. After cooling, 1.1 g. of brown solid precipitated. This crude material was recrystallized, with the help of Darco, from 130 ml. of 1 N hydrochloric acid; 0.8 g. (45%) of light yellow needles were obtained, m.p. 328° (dec.). (Found: C, 57.2; H, 4.4; N, 22.0; S, 13.0. $C_{12}H_{10}N_4S \cdot \frac{1}{2}H_2O$ requires C, 57.3; H, 4.4; N, 22.3; S, 12.8.)

2-Methyl-8-phenylpurine (XIX).

To 60 ml. of water, containing 1.5 g. of Davison sponge nickel (Grade 986) (12) was added 0.5 g. of 2-methyl-6-mercapto-8-phenyl-purine, and the mixture was refluxed for 2 hours. At the end of this time the nickel was filtered and washed with 30 ml. of boiling water. The combined filtrate and washings on cooling deposited 0.2 g. (47.8%) of white needles, m.p. 256-258°. (Found: C, 68.3; H, 5.1; N, 26.5. $C_{12}H_{10}N_4$ requires C, 68.6; H, 4.8; N, 26.7.)

Paper Chromatography.

The R_f values of both the purines and the pyrimidines were determined by ascending paper chromatography using Whatman No. 1 paper. The solvents used were methanol: concentrated hydrochloric acid: water--70:20:10 v/v (Solvent A) and n-butanol: 2 N ammonium hydroxide: ethanol - 20:5:2 v/v (Solvent B).

Ultraviolet absorption spectra.

The quantitative ultraviolet absorption spectra of both the pyrimidines and purines synthesized were measured at pH 1 (0.1 N hydrochloric acid), pH 7 (0.1 N sodium chloride), and pH 13 (0.1 N sodium hydroxide). The pH was monitored with a Beckman Model G pH meter, and the maximum deviation of pH values was ± 0.20 unit. The pH 7 solution was made by mixing equal volumes of 0.1 N hydrochloric acid solution and 0.1 N sodium hydroxide solution and adjusted to the correct pH. The pyrimidines and purines could not be dissolved directly in 0.1 N sodium chloride. A Cary model 11 spectrophotometer, employing 1 cm. quartz cells, was used.

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